John von Neumann Institute for Computing

Polarized Atomic Orbitals for Linear Scaling Methods

G. Berghold, J. Hutter, M. Parrinello

published in

Modern Methods and Algorithms of Quantum Chemistry,
J. Grotendorst (Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 2, ISBN 3-00-005746-3, p. 53, 2000.

http://www.fz-juelich.de/nic-series/

Polarized atomic orbitals for linear scaling methods

G. Berghold[1], J. Hutter[2] and M. Parrinello[1]

[1] Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

[2] Institute of Organic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

We present a modified version of the polarized atomic orbital (PAO) method of Lee and Head-Gordon [1] to construct minimal basis sets optimized in the molecular environment. The minimal basis set derives its flexibility from the fact that it is formed from atom-centered linear combinations of a larger set of atomic orbitals. This approach significantly reduces the number of independent variables that are to be determined during a calculation, while retaining most of the essential chemistry resulting from the admixture of higher angular momentum functions.

Furthermore, we combine the PAO method with linear scaling algorithms. We use the Chebyshev polynomial expansion method of Goedecker and Teter [2] and the canonical purification of the density matrix developed by Palser and Manolopoulos [3]. This scheme seems to overcome one of the major drawbacks of standard approaches for large nonorthogonal basis sets, namely numerical instabilities resulting from ill-conditioned overlap matrices. We find that the condition number of the PAO overlap matrix is independent from the condition number of the underlying extended basis set and consequently no numerical instabilities are encountered.

Various applications are shown to confirm this conclusion and to compare the performance of the PAO method against extended basis set calculations.

[1] M. S. Lee and M. Head-Gordon, J. Chem. Phys., **107**, 9085, (1997).

[2] S. Goedecker and M. Teter, Phys. Rev. B **51**, 9455 (1995).

[3] A. H. R. Palser and D. E. Manolopoulos, Phys. Rev. B **58**, 12704 (1998).